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Synthesis of a structured material based on compact spheres coated with Zn or Mg spinel

Sonia Bocanegra*, Adriana Ballarini, Osvaldo Scelza, Sergio de Miguel

INCAPE, Fac. de Ingeniería Química, Univ. Nac. del Litoral, CONICET, Santiago del Estero 2654, Santa Fe C.P.3000, Argentina.

Abstract

In this work, a synthesis method of coating with thin layers of MgAl_2O_4 or ZnAl_2O_4 over $\alpha\text{-Al}_2\text{O}_3$ spheres were developed. The method consisted in the deposition of a primer of bohemite on the spheres, followed by the impregnation with a solution of Mg or Zn nitrates, and further thermal treatments in order to obtain MAl_2O_4 (M: Mg or Zn). This method was modified to improve the thickness and purity of the layer material. With this method, layers of uniform and adequate thickness and good adhesion were achieved. Pt catalysts prepared with these materials as supports displayed good catalytic performances in the n-butane dehydrogenation reaction, especially those obtained with purified supports.

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Keywords: structured materials; zinc spinel, magnesium spinel, thin films, catalytic properties.

1. Introduction

The monoolefins production is a very important branch of petrochemical industry, since they are used for the production of polymers, alcohols, naphtha additives, etc. The catalytic production of monoolefins by dehydrogenation of n-alkanes presents advantages with respect to traditional thermal cracking process. The use of supports of metallic catalysts of high surface area, low acidity and good interaction with metals is very important for this kind of reactions carried out at high temperatures to decrease side reactions as alkane cracking and olefin polymerization. In this way, the use of magnesium and zinc spinels as supports presents advantages due to their low acidity and good interaction with the supported metals, as it was informed by Armendáriz et al. (2001), Bocanegra et

* Corresponding author. Tel.: +54-0342-4555279; fax: +54-0342-4531068.

E-mail address: sbocane@fiq.unl.edu.ar

al. (2004), Vu et al. (2011) and Ballarini et al. (2013).

The production of ceramic coating materials is an area of great development and dynamism due to their applications in aeronautical and naval industries, in high speed industrial applications for equipment in steel production and energy creating process equipment, for high and low voltage dielectric applications, in protective coating against the corrosion of diverse materials, between other uses. However, the use of different coating techniques in the preparation of structured materials for catalysis is an area of recent development. These materials have acquired importance in the last years due to the advantages in the mass and heat transfer in fast reactions carried out at high temperatures, like catalytic dehydrogenation of hydrocarbons as it was reported by Groppi et al. (2001) and Cristiani et al. (2009).

There are a lot of bibliography about coating of oxides metallic in foams, honeycombs, tubes, plates, etc. (see the review of Meille et al. (2006)), but there are practically no studies concerning to coating in spherical symmetry (Karches et al. (2002) and Ballarini et al. (2010)). Besides, there are very few papers about coating with magnesium spinel as it was reported by Browne et al. (2009), Saberi et al. (2009) and Cristiani et al. (2010) and no bibliography with respect to coating with zinc spinel. Hence, the coating method developed in this study is original, as well as its application to metallic catalyst supports. The purpose of this work is the production of a uniform thin layer of MgAl_2O_4 and ZnAl_2O_4 on a compact nuclei of $\alpha\text{-Al}_2\text{O}_3$ by coating first with a primer of bohemite suspension, then impregnation with solution of zinc (or magnesium) salt, followed by calcination at high temperature. This layer needs to have both suitable conditions of thickness and resistance to the cracking and peeling in the operation conditions of the material.

2. Materials Synthesis

For the preparation of the materials by coating, the starting material were spheres ($\phi = 2$ mm) of commercial $\alpha\text{-Al}_2\text{O}_3$ ($\text{Sg} = 4.7 \text{ m}^2\text{g}^{-1}$) and commercial $\text{AlO}(\text{OH})$ (Disperal P2), both provided by SASOL company, and 99 % $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (Sigma Aldrich), 99 % $\text{Zn}(\text{NO}_3)_2$ (Fluka). $6 \text{H}_2\text{O}$, 99 % $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (Sigma Aldrich).

2.1. Pretreatment of $\alpha\text{-Al}_2\text{O}_3$ spheres

Spheres were treated at room temperature with HCl 1 M solution for 24 h (ratio of 1.4 mL HCl . g^{-1} $\alpha\text{-Al}_2\text{O}_3$) in order to develop roughness at the external surface. Then the spheres were rinsed with distilled water until neutral pH followed by a drying step at 120°C for 24 h.

2.2. Method bohemite-nitrate (BN)

i) Deposition of a primer of bohemite ($\text{AlO}(\text{OH})$): The dip coating method was used to deposit bohemite gel on the spheres of $\alpha\text{-Al}_2\text{O}_3$. The spheres were submerged (with stirring) in a stable dispersion of bohemite (15 wt%). This process was carried out using the device showed in Figure 1. Four impregnations of 20 min each one at 150 rpm were carried out, with a drying step (with warm air flow) after each impregnation. After this process, the spheres with primer were dried in furnace during 24 h at 120°C .

ii) Impregnation with nitrate solution: The spheres with bohemite primer were impregnated with 0.5 M solution of $\text{M}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ($\text{M} = \text{Mg}$ or Zn) during 6 h. The volume of solution was calculated taking account the weight of $\text{AlO}(\text{OH})$ deposited on the spheres for obtaining a molar ratio $\text{M}/\text{Al} = 2$. Then, the spheres were dried in furnace during 12 h at 120°C .

iii) Spinel formation: After magnesium (or zinc) nitrate impregnation, the spheres were calcined in air flow ($100 \text{ ml} \cdot \text{min}^{-1}$) for 4 h at 850°C in order to obtain the corresponding spinel.

2.3. Method bohemite-nitrate advanced (BNA)

i) Deposition of a primer of bohemite ($\text{AlO}(\text{OH})$): The dip coating method was used to deposit bohemite gel on the spheres of $\alpha\text{-Al}_2\text{O}_3$. The spheres were submerged (with agitation) in a stable dispersion of bohemite (5 wt

%). This process was carried out using the device showed in Figure 1. Four impregnations of 20 minutes each one at a 150 rpm were carried out, followed by a drying step (with warm air flow) after each impregnation. This process was repeated with bohemite dispersion of a 10 wt %, and then with bohemite dispersion of 15 wt %. After this process, the spheres with primer were dried in furnace during 24 h at 120 °C.

The items ii) and iii) are similar to those described in the BN method.

2.4. Method bohemite-nitrate advanced with purification (BNAP)

The items i), ii) and iii) are similar to those described in BNA method. iv) Purification: The spheres coated with spinel were submitted to a purification method in order to eliminate the residues of MO (M = Mg or Zn) in the coating material. The step was carried out with a 1 M $(\text{NH}_4)_2\text{CO}_3$ solution. The coated spheres were submerged (with mild stirring) in the $(\text{NH}_4)_2\text{CO}_3$ solution during 20 min and then filtered. This process was repeated five times. Finally, the spheres were rinsed with excess of distilled water and dried in furnace for 24 h at 120 °C.

3. Materials characterization

3.1. Analysis by SEM

In order to observe the aspect and thickness of the formed layer, analysis by scanning electronic microscope (SEM) were carried out. The instrument was a JSM-35C, JEOL model, equipped with SemAfore digital image acquisition system. The observations were performed under the way of images of secondary electrons using an acceleration voltage of 20 kV. The samples were adhered with silver paint on metallic slides and coated with a thin layer of gold by sputtering to give them conductivity before the observation.

3.2. Composition by DRX

The composition of layers was analyzed by X-ray diffraction experiments performed at room temperature in a Shimadzu model XD3A instrument using $\text{CuK}\alpha$ radiation ($\lambda=1,542\text{\AA}$), generated at 30 kV and a current of 30 mA. The sample was obtained as a residual powder coming from the calcination step of coated spheres (see item iii) of BN and BNA methods). In case of the BNAP method, the sample of powder was obtained scraping carefully the layer of the spheres after the purification with a scalpel and a magnifying glass.

3.3. Stability tests

Experiments of stability of the layers deposited on the structured materials were carried out by placing a certain mass of spheres in a beaker and then distilled water enough to cover completely the spheres was added. The beaker with the spheres was put in an ultrasonic equipment (Ultrasonic cleaner Cleanson 200 W), and sonicated during 20 min. Then the spheres were dried in furnace during 24 h and its weight was determined in order to establish the weight loss. This experiment was carried out using as a model the test developed by Meille et al. (2005).

3.4. Preparation of Pt catalysts and test reaction

The coated spheres were used as catalytic supports. They were impregnated with a solution of chloroplatinic acid during 6 h at room temperature in order to obtain a catalyst with 0.3 wt % Pt, and then they were dried in a furnace at 100 °C and calcined during 3 h at 500 °C.

The catalysts were tested in the n-butane dehydrogenation reaction, carried out in a quartz continuous flow reactor at 530 °C for 2 h. The reactor (with a catalyst weight of 0.200 g) was fed with 18 mL min^{-1} of the reactive mixture (n-butane + hydrogen, $\text{H}_2/\text{n-C}_4\text{H}_{10}$ molar ratio = 1.25). Prior to the reaction, catalysts were reduced “in situ” at 530 °C under flowing H_2 for 3 h. The reactor effluent was analyzed in a GC-FID equipment with a packed column (1/8” x 6 m, 20 wt% BMEA on Chromosorb P-AW 60/80), which was kept at 50°C during the analysis. With this

analytical device, the amounts of methane, ethane, ethylene, propane, propylene, n-butane, 1-butene, cis-2-butene, trans-2-butene and 1,3 butadiene were measured.

4. Results and discussion

The objective of the work is the formation of a thin porous layer of MgAl_2O_4 and ZnAl_2O_4 , of uniform thickness and resistant to cracking and peeling, over the nucleus of $\alpha\text{-Al}_2\text{O}_3$.

Table 1. Increase of weight of coated spheres and thickness of layers determined by SEM

	Increase of weight (%)	Average thickness of layer (μm)
$\alpha\text{-Al}_2\text{O}_3$ spheres coated MgAl_2O_4 BN method	13	11
$\alpha\text{-Al}_2\text{O}_3$ spheres coated MgAl_2O_4 BNA method	19	30
$\alpha\text{-Al}_2\text{O}_3$ spheres coated MgAl_2O_4 BNAP method	16	13
$\alpha\text{-Al}_2\text{O}_3$ spheres coated ZnAl_2O_4 BN method	11	10
$\alpha\text{-Al}_2\text{O}_3$ spheres coated ZnAl_2O_4 BNA method	17	19
$\alpha\text{-Al}_2\text{O}_3$ spheres coated ZnAl_2O_4 BNAP method	15	12

Table 1 shows the results corresponding to the increase of weight and thickness of the deposited layers on spheres. An increase of 13 % on spheres weight after coating with MgAl_2O_4 by BN method can be seen in Table 1. However a higher increase of the weight of the deposited layer of the MgAl_2O_4 was achieved by the application of the BNA method (19 %). After the purification with ammonium carbonate (BNAP method), the weight of spheres coated with MgAl_2O_4 decreases from 19 to 16%. Similar results can be observed for the coating with ZnAl_2O_4 by the three methods (see Table 1). In conclusion, the BNA method increases the weight of the layer of MgAl_2O_4 or ZnAl_2O_4 deposited on the $\alpha\text{-Al}_2\text{O}_3$ sphere with respect to the original BN method. Besides, the purification process with ammonium carbonate solution slightly decreases the weight of the coated spheres.

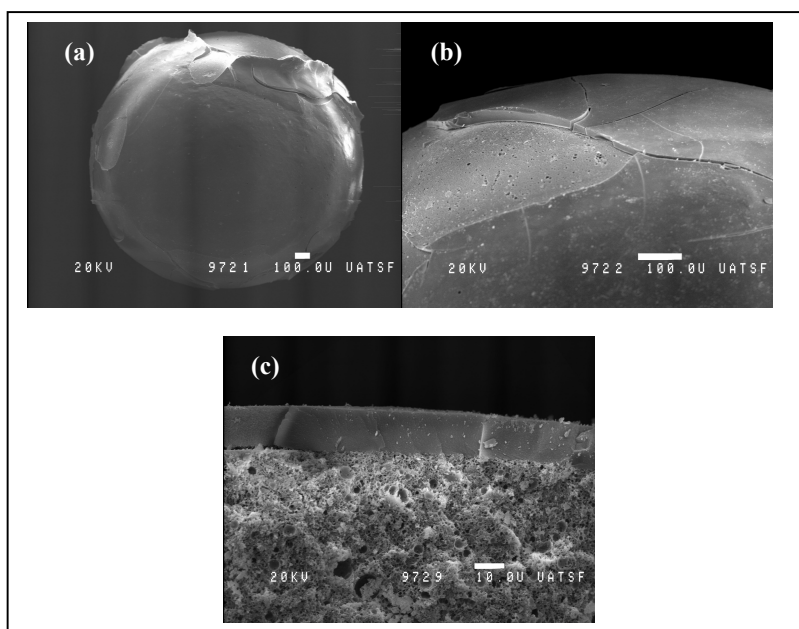


Fig. 1. SEM microphotographs of $\alpha\text{-Al}_2\text{O}_3$ spheres coated by BN method with MgAl_2O_4 : (a) View of a coated sphere, (b) enlarging of a sector of the coated sphere, (c) View of a cut of the sphere.

Figures 1(a) and 1(b) show a sphere coated by BN method with $\text{Mg Al}_2\text{O}_4$. It can be seen a uniform layer of material, with a thickness of about $13\ \mu\text{m}$ (Figure 1 (c)). Besides, effects of cracking are observed in determined zones of the sphere, at the position where the sphere was set during the drying treatment.

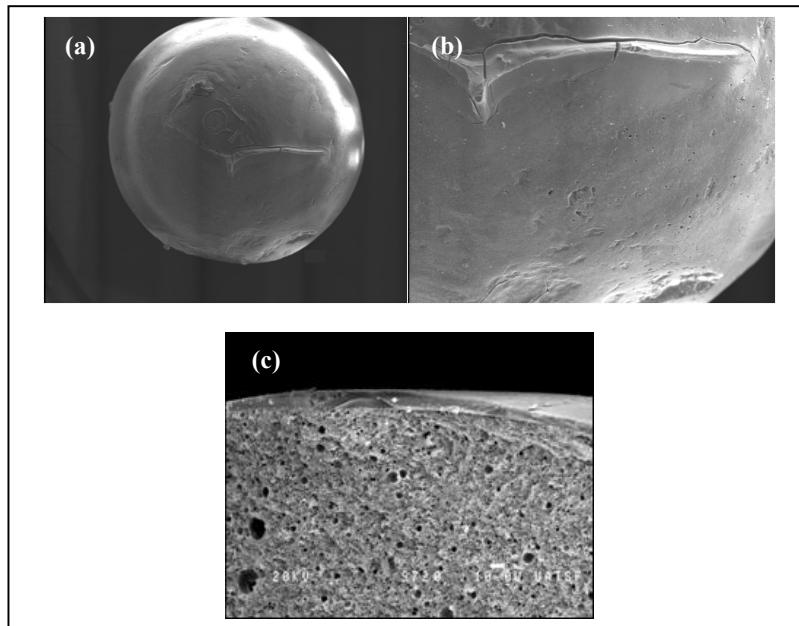


Fig. 2. SEM microphotographs of $\alpha\text{-Al}_2\text{O}_3$ spheres coated by BN method with $\text{Zn Al}_2\text{O}_4$: (a) View of a coated sphere, (b) enlarging of a sector of the coated sphere, (c) View of a cut of the sphere.

Figure 2, corresponding to coating with ZnAl_2O_4 by BN method, shows that there is a thin layer of material covering the sphere nucleus (Figure 2(a) and Figure 2(b)), with a thickness of about $11\ \mu\text{m}$ (Figure 2 (c)). In a similar way than in Figure 1, the cracking effects in the layer are also observed, due to the contact point of the sphere during the drying step

The SEM microphotographs of spheres coated by BNA method with MgAl_2O_4 can be observed in Figure 3. The sphere uniformly covered is displayed in Figure 3(a). In Figure 3(b) and 3(c), a layer of deposited material on the sphere of about $20\text{--}40\ \mu\text{m}$ of thickness is clearly shown.

In Figure 4, coated spheres by BNA method with ZnAl_2O_4 can be observed. The uniform aspect of the covered sphere is displayed in Figure 4 (a). The thickness of layer on the sphere can be seen in Figures 4 (b) and 4 (c). This film has a thickness of about $15\text{--}24\ \mu\text{m}$.

Figure 5 shows SEM images of the spheres coated by BNA method (MgAl_2O_4) after the purification treatment with ammonium carbonate solution. In Figure 5(a) it can be seen that the sphere remained almost completely covered with the layer, but some small fractions of the layer are absent, thus meaning that the coated sphere suffered a slight peeling. The cut of the sphere in Figure 5(c) shows a layer of about $13\ \mu\text{m}$ of thickness.

In Figure 6, SEM microphotographs of structured material obtained by coating with ZnAl_2O_4 (BNAP method) are shown. A uniformly and completely covered sphere is displayed in Figure 6(a). In Figures 6(b) and (c), the microphotographs of the cuts of a coated sphere show clearly the layer on the $\alpha\text{-Al}_2\text{O}_3$ sphere. This layer has a thickness of about $12\ \mu\text{m}$.

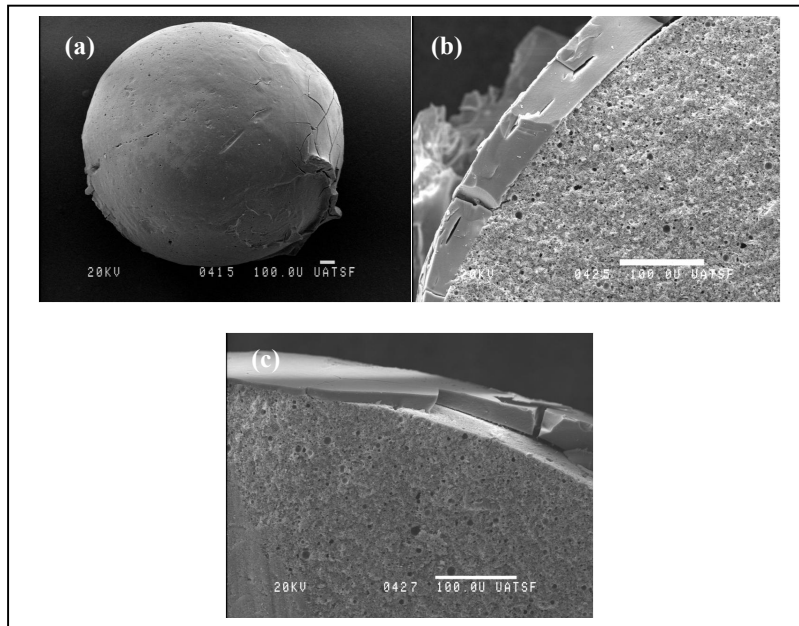


Fig. 3. SEM microphotographs of α - Al_2O_3 spheres coated by BNA method with MgAl_2O_4 : (a) View of a coated sphere, (b) View of a cut of the coated sphere and (c) View of other cut of a coated sphere.

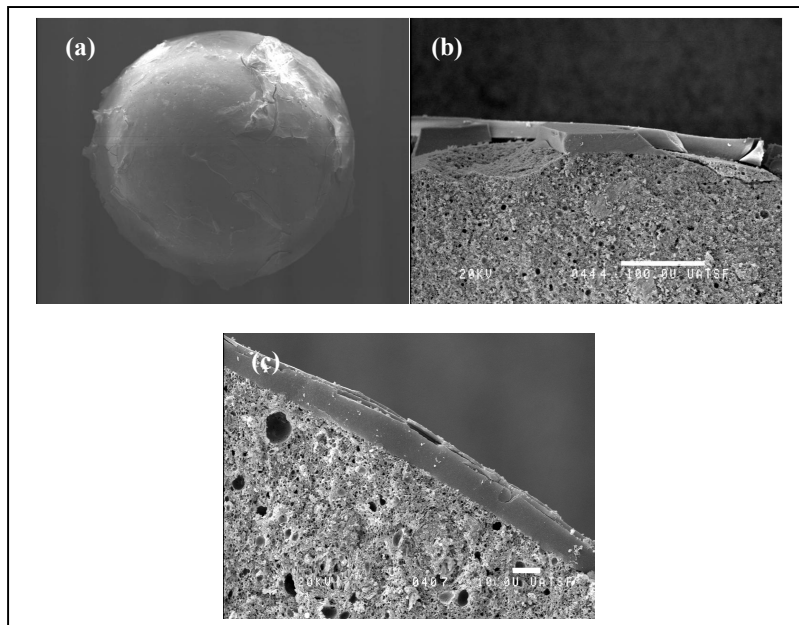


Fig. 4. SEM microphotographs of α - Al_2O_3 spheres coated by BNA method with ZnAl_2O_4 : (a) View of a coated sphere, (b) View of a cut of the coated sphere and (c) View of other cut of a coated sphere.

SEM results display that the BNA method increases the thickness of the layer deposited in the α - Al_2O_3 spheres compared to BN method. This fact is in accordance with the increase of weight of coated spheres in BNA method with respect to the BN one shown in Table 1. The purification step (BNAP method) decreases the thickness of the layer deposited in the spheres by BNA method, such as it can be observed in Table 1.

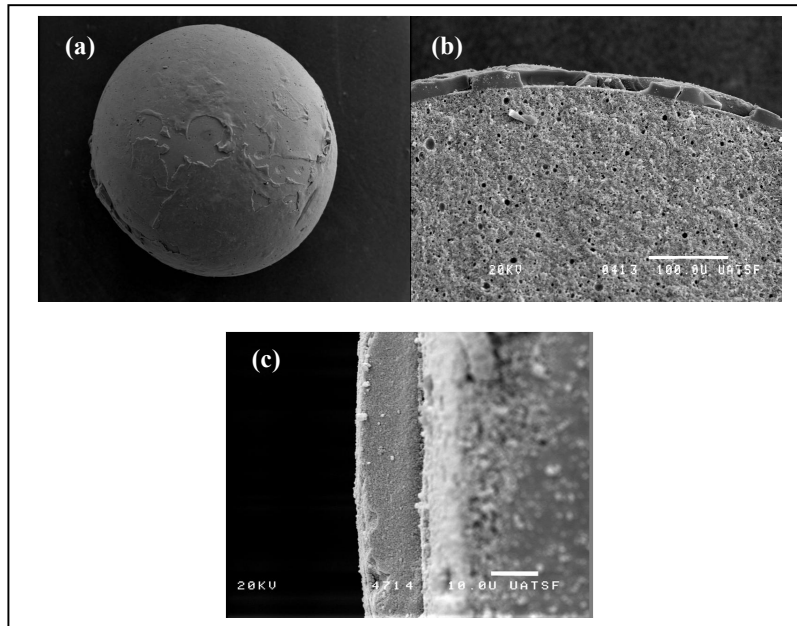


Fig. 5. SEM microphotographs of α - Al_2O_3 spheres coated by BNAP method with MgAl_2O_4 : (a) View of a coated sphere, (b) View of a cut of the coated sphere and (c) View of other cut of a coated sphere.

For all the samples, the results of stability experiments of the different layers of the structured materials showed a loss of weight lower than 0.4 %. The formula for the calculus was:

$$\% \text{ Loss weight} = \frac{\text{spheres weight} - \text{spheres weight (after ultrasonic test)}}{\text{spheres weight}} \times 100$$

These results indicate a good adhesion of the layers obtained by different methods on α - Al_2O_3 spheres.

In order to determine the formation of MgAl_2O_4 or ZnAl_2O_4 spinels in the material deposited on the spheres, diffractograms were carried out by using powders of the layer of coated spheres (see experimental section), and the results are displayed in Figures 7 and 8.

With respect to the coating by BN method with MgAl_2O_4 , Figure 7(a) displays the formation of the magnesium spinel (MgAl_2O_4), but peaks corresponding to the MgO are also present in the layer, due to the incomplete reaction of the spinel synthesis. In the case of the coating by BN method with ZnAl_2O_4 , Figure 8(a) shows the formation of the zinc spinel (ZnAl_2O_4) and also the presence of ZnO . When the coating was carried out by the BNA method (MgAl_2O_4), the intensity of the peaks corresponding to MgO decreases drastically (Figure 7 b). Hence, only traces of this oxide remain in the sample. In the diffractogram corresponding to coating with ZnAl_2O_4 by BNA method (Figure 8(b)), a slight decrease of the peak intensity of ZnO can be also seen. These residual oxides, MgO or ZnO , in the layer could affect the behavior of these materials in their applications, e.g. as supports of catalysts. Hence the purification treatment would be very important to obtain a coating formed exclusively by MgAl_2O_4 or ZnAl_2O_4 .

spinel. It was not possible to carry out the analysis by X-ray diffraction of the layer deposited in the spheres by the BNAP method because the scraped of the layer of the spheres (see experimental section) drags small amounts of α - Al_2O_3 from the nucleus, which have very intense diffraction peaks that overlap with those of ZnAl_2O_4 or MgAl_2O_4 .

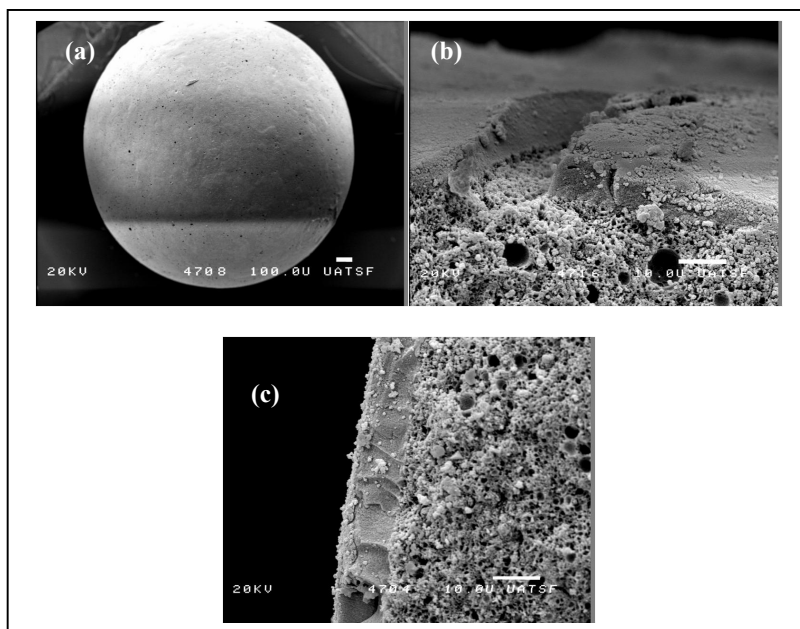


Fig. 6. SEM microphotographs of α - Al_2O_3 spheres coated by BNAP method with ZnAl_2O_4 : (a) View of a coated sphere, (b) View of a cut of the coated sphere and (c) View of other cut of a coated sphere.

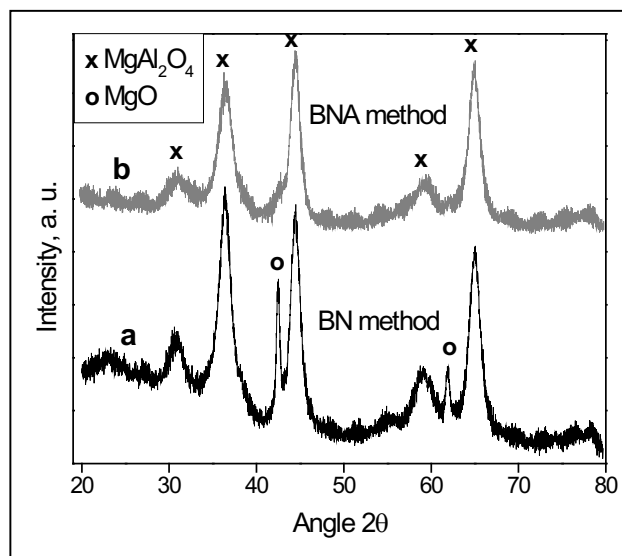


Fig. 7. Diffractograms of the powder from the layers obtained by the BN (a) and BNA (b) methods (MgAl_2O_4).

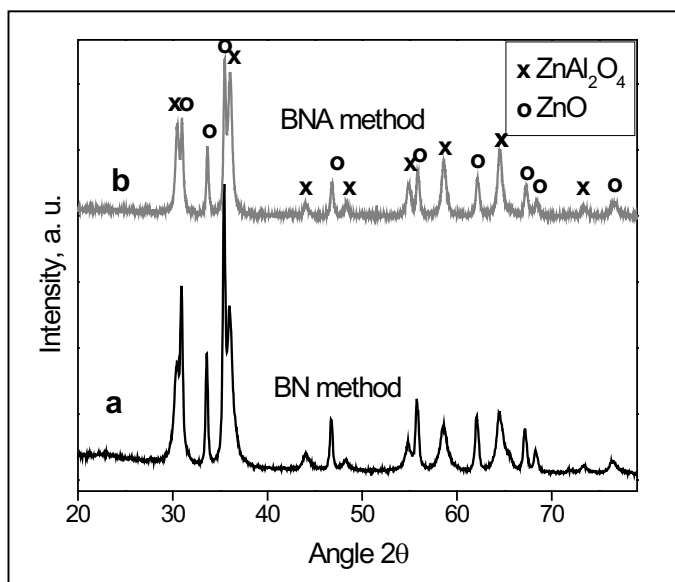


Fig. 8. Diffractograms of the powder from the layers obtained by the BN (a) and BNA (b) methods (ZnAl_2O_4).

In order to compare the performance of these materials as supports, Pt catalysts supported on the different structured supports, synthesized by the three techniques (BN, BNA and BNAP), were evaluated in the reaction of n-butane dehydrogenation to produce butenes. The results from Table 2 display good catalytic behaviors of the different coated catalysts. Two general trends can be observed: i) the yields to butenes increase in the following order respect to the synthesis method of the structured support: $\text{BN} < \text{BNA} < \text{BNAP}$. ii) The structured catalysts coated with MgAl_2O_4 have higher yields to butenes than those catalysts coated with ZnAl_2O_4 . In this sense, the $\text{Pt/MgAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ (BNAP) catalyst displays the best catalytic behavior. In conclusion, the improvement of coating method as regards the thickness and purity of the layer enhance the catalytic performance of structured supports. These facts can be explained taking into account that the support influences both the size and shape of Pt the metallic particles, this being very important for the catalytic behavior. Besides there can be interactions between metal and support, which could affect the catalytic activity. In this case, the higher the thickness of the layer, the higher the surface available to deposit the metal, and thus the higher the metallic dispersion. With respect to the importance of the purity of spinels, the presence of ZnO in the layer could affect the catalytic function of the platinum, due to the probable formation of Pt-Zn alloys, which deactivate the metallic phase of Pt catalysts supported in ZnAl_2O_4 with impurities of ZnO , like it was informed by Pakhomov et al. Besides, the use of MgO as a support of monometallic Pt catalysts did not show good catalytic behavior in this type of reactions as it was studied by de Miguel et al.

Table 2. Yields to butenes (Y) at different reaction times for the Pt catalysts synthesized with the structured supports. Yield to butenes = (% conversion of n-butane x % selectivity to butenes)/100

	Y at 10 min (%)	Y at 60 min (%)	Y at 120 min (%)
α -Al ₂ O ₃ spheres coated MgAl ₂ O ₄ BN method	15.8	11.5	10.4
α -Al ₂ O ₃ spheres coated MgAl ₂ O ₄ BNA method	18.5	15.0	14.1
α -Al ₂ O ₃ spheres coated MgAl ₂ O ₄ BNAP method	21.7	19.7	19.2
α -Al ₂ O ₃ spheres coated ZnAl ₂ O ₄ BN method	16.4	10.8	10.4
α -Al ₂ O ₃ spheres coated ZnAl ₂ O ₄ BNA method	15.8	13.5	13.0
α -Al ₂ O ₃ spheres coated ZnAl ₂ O ₄ BNAP method	18.6	16.7	16.7

5. Conclusions

The developed method of coating with thin layer of MgAl₂O₄ or ZnAl₂O₄ over the α -Al₂O₃ spheres was successful. It achieved a layer of uniform and adequate thickness and, besides, good adhesion. The troubles due to presence of residues of ZnO and MgO in the layers by the incomplete reaction of spinels formation were solved with the purification step after the coating process. The Pt catalysts prepared with these materials as supports displayed good catalytic performances in the n-butane dehydrogenation reaction, especially the catalysts obtained with purified supports.

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